

PATENT SPECIFICATION

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Date of Application and filing Complete Specification: July 8, 1955.

No. 19854/55.

Application made in Germany on July 12, 1954.

Application made in Germany on Sept. 15, 1954.

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Complete Specification Published: March 19, 1958.

Index at acceptance:—Classes 1(2), D1B, E(1A2: 4A1: 6: 8); and 2(1), K3.

International Classification:—C01c, C07c.

COMPLETE SPECIFICATION

SPECIFICATION NO. 792,017

The inventor of this invention in the sense of being the actual deviser thereof within the meaning of Section 16 of the Patents Act, 1949, is Dieter Goerrig, of 17, Bachstrasse, Lohmar (Siegkreis) Germany, a German citizen.

THE PATENT OFFICE,
2nd April, 1958

DE 04247/1(5)/3596 150 3/58 R

15 wherein a carbide, cyanide, cyan-
amide, phosphide, silicide, or boride of one of
these metals is reacted with hydrogen under
such conditions and for such a period that a
substantial amount of the hydride of the metal
is formed. The reaction proceeds in such
20 manner that both the metal constituent and the
non-metallic constituent of the compound
reacted with hydrogen is hydrogenated, i.e.
that a metal hydride and also a hydrogen com-
pound of the non-metallic constituent is
25 obtained.

The invention will first of all be described
in detail by way of example by reference to
the reaction of calcium carbide with hydrogen.

30 Calcium carbide reacts with hydrogen at all
the temperatures investigated. The primary
product of the reaction appears to be C_2H_2 , as
well as CaH_2 . Depending on the conditions of
the experiment, the acetylene remains un-
35 changed, decomposes into carbon black and
hydrogen, forms diacetylene or other polymers,
or is hydrogenated to form ethylene, ethane or
methane.

40 The speed of reaction between calcium
carbide in the usual commercial form and
hydrogen at temperatures up to 1000°C . (with-
out pressure) or up to 600°C . (with a hydro-
gen pressure of 500 atm.) is so low that it does
not appear to be readily possible for the
45 hydride to be produced on an industrial scale.
However, various measures can be used for
increasing the speed of reaction.

An appreciable increase in the speed of
reaction is produced by increasing the surface
[Price]

(100 μ —10 mm). These requirements limit
the other possibilities, thus whilst material
having a particle size of 1 μ can be reacted
according to all the Examples hereinafter set
forth, material having a particle size of 10
mm can be reacted, with the formation prac-
tically only of methane under conditions of
super-atmospheric pressure and elevated tem-
perature, for example 60 atmospheres and
900 $^\circ\text{C}$.

Furthermore, a large number of substances,
for example N_2 , S, I $_2$, NH_3 , H_2S , HI, HgI_2 ,
 CaI_2 , MgI_2 , Na_2S , CaS and Na, act as cata-
lysts. These substances either themselves enable
calcium carbide to react or they change wholly
or partly (giving an equilibrium mixture) into
compounds which enable calcium carbide to
react.

By means of these measures, the speed of
reaction is increased to such an extent that it
is not necessary to use high temperatures or
pressures for economically converting the
carbide into the hydride; this is not even
necessary when a technical commercial prod-
uct containing, for example, 80% of CaC_2
is used instead of a pure calcium carbide.

Higher temperatures and pressures not only
raise the speed of reaction but also modify the
nature of the reaction products:

a) At low temperatures (about 0 — 300°C),
low pressures (about 0.05 — 5 atm.) and high
flow velocities of the hydrogen the acetylene,
considered as primary product of the reaction,
is substantially unchanged.

b) At temperatures which are still relatively

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COMPLETE SPECIFICATION

Process for the Production of Metal Hydrides

We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, of Leverkusen - Bayerwerk, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of metal hydrides.

It provides a process for the production of hydrides of the metals calcium, strontium, barium, magnesium, lithium, sodium and potassium, wherein a carbide, cyanide, cyanamide, phosphide, silicide, or boride of one of these metals is reacted with hydrogen under such conditions and for such a period that a substantial amount of the hydride of the metal is formed. The reaction proceeds in such manner that both the metal constituent and the non-metallic constituent of the compound reacted with hydrogen is hydrogenated, i.e. that a metal hydride and also a hydrogen compound of the non-metallic constituent is obtained.

The invention will first of all be described in detail by way of example by reference to the reaction of calcium carbide with hydrogen.

Calcium carbide reacts with hydrogen at all the temperatures investigated. The primary product of the reaction appears to be C_2H_2 , as well as CaH_2 . Depending on the conditions of the experiment, the acetylene remains unchanged, decomposes into carbon black and hydrogen, forms diacetylene or other polymers, or is hydrogenated to form ethylene, ethane or methane.

The speed of reaction between calcium carbide in the usual commercial form and hydrogen at temperatures up to 1000°C . (without pressure) or up to 600°C . (with a hydrogen pressure of 500 atm.) is so low that it does not appear to be readily possible for the hydride to be produced on an industrial scale. However, various measures can be used for increasing the speed of reaction.

An appreciable increase in the speed of reaction is produced by increasing the surface

of the carbide used by a grinding or other comminuting treatment of the commercial form of the carbide. Moreover, the speed of reaction is increased to a remarkable extent by comminuting under a good vacuum or in a pure inert gas atmosphere. In practice, to ensure that the entire mass takes part in the reaction using such specially comminuted material, requires at least a temperature of 500°C . with material of very small particle size ($1\ \mu$), $600\text{--}700^\circ\text{C}$. with material of medium particle size ($5\text{--}80\ \mu$), and $780\text{--}980^\circ\text{C}$. with material of large particle size ($100\ \mu\text{--}10\ \text{mm}$). These requirements limit the other possibilities, thus whilst material having a particle size of $1\ \mu$ can be reacted according to all the Examples hereinafter set forth, material having a particle size of 10 mm can be reacted, with the formation practically only of methane under conditions of super-atmospheric pressure and elevated temperature, for example 60 atmospheres and 900°C .

Furthermore, a large number of substances, for example N_2 , S, I_2 , NH_3 , H_2S , HI, HgI_2 , CaI_2 , MgI_2 , Na_2S , CaS and Na, act as catalysts. These substances either themselves enable calcium carbide to react or they change wholly or partly (giving an equilibrium mixture) into compounds which enable calcium carbide to react.

By means of these measures, the speed of reaction is increased to such an extent that it is not necessary to use high temperatures or pressures for economically converting the carbide into the hydride; this is not even necessary when a technical commercial product containing, for example, 80% of CaC_2 is used instead of a pure calcium carbide.

Higher temperatures and pressures not only raise the speed of reaction but also modify the nature of the reaction products:

a) At low temperatures (about $0\text{--}300^\circ\text{C}$.), low pressures (about $0.05\text{--}5\ \text{atm.}$) and high flow velocities of the hydrogen the acetylene, considered as primary product of the reaction, is substantially unchanged.

b) At temperatures which are still relatively

low (about 200—400°C.), low to moderate pressures (about 0.5—50 atm.) and moderate flow velocities of hydrogen, a large part of the gaseous reaction product formed is ethylene.

5 c) At a temperature in the region of 400—500° C. and at a low pressure (up to about 1 atm.) a large part of the acetylene changes into diacetylene, another part into carbon black and hydrogen, a small part into ethane and methane and another very small part into ethylene.

10 d) Reaction at 400—500°C. and a pressure of 500 atm. produces no carbon black at all, but a very large amount of ethane, a considerable amount of methane, traces of acetylene and no ethylene.

15 e) At normal pressure, a temperature of 500—600°C. and a low flow velocity, carbon black is mainly formed in addition to the calcium hydride, as well as a small amount of C_2H_2 , CH_4 , and C_2H_4 .

20 f) At 600—700°C., predominantly CH_4 is formed as well as carbon black and ethane at normal pressure and with a moderate flow velocity.

25 g) At 700—800°C., normal pressure and with a moderate flow velocity, practically only methane is formed.

30 The examples given under a to g are only intended to show that a wide variety of different reaction products can be obtained in addition to calcium hydride, depending on the conditions chosen for the experiment. It does not mean that only one or other of the by-products can be produced at a specified temperature or a specified pressure. Variations in the fineness of grinding, the nature of the reaction vessel, the movement of the reaction mass and catalyst, and above all the gas velocity, produce entirely different results, both as regards quality and quantity.

35 h) Thus, in contrast to the example given under g), when a temperature of about 800°C. and a pressure of 500 atm. is used, almost the only product formed is acetylene in addition to a small amount of methane, if the flow velocity is chosen to be so high that the waste gas consists of more than 90% of hydrogen and the said waste gas cools after the reaction zone.

40 Since the last fractions of calcium carbide (substantially those between a conversion of 80% and more than 95% of the theoretical) react better at a high temperature than at a low temperature, it is advisable in certain cases to use a two-stage process, for example a reaction at 400°C. to form calcium hydride and acetylene with a yield of up to 80% of the theoretical, and a subsequent reaction at 800°C. up to a conversion higher than 95% of the theoretical.

45 Depending on the purpose to which the calcium hydride is subsequently to be put, the said calcium hydride can be used in the form of the crude reaction product of the hydrogenation, after a re-melting process, or, if ultra-pure products are required, after a distillation process (over calcium metal).

By means of the process of the invention, calcium hydride can be produced at a fraction of its former cost.

70 The carbides of strontium, barium, magnesium, lithium, sodium and potassium also behave in the same manner as described above in respect of calcium carbide.

75 Furthermore, the cyanides, cyanamides, phosphides, silicides and borides behave in the same manner as the carbides; when reacted with hydrogen, they form in analogous manner the metal hydrides as well as the hydrogen compounds of the non-metallic constituents; for example boron hydride, silicon hydride and phosphorus hydride is obtained as a secondary product.

80 The following Examples, wherein percentages of gas are by volume and of solids are by weight further illustrate the invention.

EXAMPLE 1.

85 Hydrogen is introduced at 500°C. and over a period of 2 hours into an autoclave containing 250 g. of an approximately 80% calcium carbide ground in an argon atmosphere, until the pressure remains constant at 600 atm. gauge. The gas, having a composition of about 60% C_2H_2 , about 40% CH_4 , and about 0.1% of C_2H_4 , H_2 and C_2H_6 , is drawn off and the autoclave is again placed under hydrogen pressure until a pressure of 600 atm. is constantly maintained. The reaction product removed after cooling is a practically white powder generates with water a gas containing 4—5% of acetylene, the remainder being hydrogen, and contains about 70% by weight of CaH_2 .

EXAMPLE 2.

100 200 g. of an approximately 80% calcium carbide ground under an argon atmosphere and 6 g. of MgI_2 are introduced into a horizontal steel tube having an internal diameter of about 50 mm., heated in an electric furnace to 750—800°C., in a stream of argon, and hydrogen is passed through after the said temperature has been reached, a waste gas velocity of 20 standard litres per hour being maintained. During the first five hours of the reaction, the methane content of the waste gas initially rises to 55% and finally drops to 45%. The waste gas also contains about 1% by volume of ethane and about 0.2% by volume of acetylene. The methane concentration falls to about 10% towards the end of the sixth hour. The experiment is then stopped. The reaction product is almost pure white in the upper parts of the reaction tube, over which there is a good flow of hydrogen, and analysis shows that the conversion is more than 90% of the theoretical. In the central and lower parts of the reaction tube, the reaction product is grey to black in colour, due to precipitated carbon

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black. The overall average conversion of the sample is 65%.

EXAMPLE 3.

The reaction vessel used is a pressure-tight apparatus comprising essentially two storage vessels which are connected by a steel tube with a diameter of 60 mm. and a built-in conveyor worm, the said tube being up to a metre in length and being able to be heated to 700°C. During the reaction, calcium carbide is fed from one storage container by means of the worm through the reaction tube and the calcium hydride formed is discharged into the other storage container. The entire apparatus is under operating pressure, while the hydrogen is constantly introduced into the reaction tube in counter-current to the carbide and the waste gas formed is discharged at the other end.

Details of three hydrogenations carried out in this way are set out under the following headings A, B and C.

EXPERIMENT A.

10 kg. of 85% pulverous calcium carbide are reacted in 5 hours in the heating zone at 680°C. and with a total pressure of 100 atmospheres, the said carbide being conveyed by the worm so as to be in the heating zone for about 20 minutes. 50% of the hydrogen is converted into methane and 15% into ethane. The solid reaction product has a calcium hydride content of 67% by weight, the loss in weight as compared with the starting material being 26%. The conversion of the calcium carbide present to calcium hydride is 90%.

EXPERIMENT B.

More of the same calcium carbide powder is hydrogenated at a temperature of 600°C. and a total atmospheric pressure of 150 atm., with a length of stay of 30 minutes. 86% of the calcium carbide is converted into calcium hydride; 40% of the hydrogen used is changed into methane and 35% into ethane.

EXPERIMENT C.

Moulded elements with a diameter of about 10 mm., prepared at a pressure of 500 kg/cm² with a pore volume of 20—30% from the above calcium carbide powder, are hydrogenated at 680°C. and a total pressure of 150 atm. with a length of stay of 15 minutes, 94% of the calcium carbide present is changed into calcium hydride, while 60% of the hydrogen used is converted into methane and 20% into ethane.

EXAMPLE 4.

380 g. of a 69% strontium carbide with 5% of C, 24% of SrO and 2% of other impurities are reacted in an autoclave in a finely ground condition (5—10 μ) at 650°C. with a stream of hydrogen at 100 to 120 atm. pressure.

326 g. of a 63% strontium hydride with 2% of total carbon as impurity are obtained, as well as a waste gas consisting of 50% of H₂, 35% of CH₄ and 15% of C₂H₆, after a length of stay of 1 hour at 650°C.

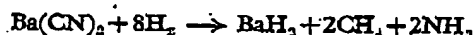
EXAMPLE 5.

450 g. of a 61% barium carbide with 4.5% of C, 33% of BaO and 1.5% of other impurities are reacted at 650°C. with a stream of hydrogen at 100 to 120 atm. pressure in an autoclave, the said carbide being in a finely ground condition (5—10 μ).

With a length of stay of one hour at 650°C., a waste gas consisting of 50% of H₂, 35% of CH₄ and 15% of C₂H₆ is obtained, as well as 395 g. of crude barium hydride with 59% by weight of BaH₂ and 0.5% of total carbon, substantially all the remainder being BaO.

EXAMPLE 6.

250 g. of a dry barium cyanide finely ground under a protective gas atmosphere are reacted at 700°C. in an autoclave at a total pressure of 150 atm. with a stream of hydrogen having an admission velocity of 200 standard litres per hour, the reaction being in accordance with the equation:



a part of the NH₃ changing into N₂ and H₂, according to its equilibrium. The waste gas, which initially consists of about 15% of CH₄ and 5% of NH₃, is practically free from CH₄, NH₃ or N₂ after 6 hours. The experiment can then be stopped. About 190 g. of a 90% BaH₂ are obtained.

EXAMPLE 7.

300 g. of a commercially available calcium cyanamide are finely ground under benzene, dried, and 250 g. of the product are reacted at 700°C. with a total pressure of 150 atm. with hydrogen flowing at the rate of 200 litres per hour. After initially strong formation of CH₄, NH₃ and N₂, the formation of NH₃ and N₂ ceases after 3 to 4 hours, while methane is formed for approximately another 3 hours from the elementary carbon. The experiment is stopped after 7 hours and yields 150 g. of a 55% CaH₂.

EXAMPLE 8.

400 g. of a 95% Li₃P are finely ground under benzene and dried in a protective gas atmosphere. 300 g. of the powder are treated at a temperature of 700°C. and a total pressure of 150 atm. with hydrogen flowing at the rate of 100 litres per hour, the treatment lasting 24 hours. The initially strong PH₃ formation subsides considerably after 8 hours and can no longer be detected towards the end of the experiment. 120 g. of an 80—85% lithium hydride are obtained.

EXAMPLE 9.

300 g. of an approximately 90% strontium silicide SrSi₂ which has been well comminuted are reacted for 16 hours at a temperature of 750°C. and a total pressure of 150 atm. gauge with hydrogen flowing at the rate of 150 litres per hour. After initially strong formation of SiH₄, the SiH₄ content of the waste gas at the end of the experiment

is less than 0.1%. Approximately 200 g. of an approximately 60% SrH_2 are obtained with a residual Si content of approximately 5%.

EXAMPLE 10.

- 5 150 g. of thoroughly fused magnesium boride with an Mg_2B_3 content of about 80% are ground under benzine, dried in a protective gas atmosphere and thereafter reacted with 200 litres per hour of hydrogen for 5
10 hours at a temperature of 700°C . and a total pressure of 180 atm. The evolution of boron hydride at the beginning of the reaction at high temperature is high, but drops after 2
15 hours; it becomes apparent again during the transition to lower temperature and higher pressure. 120 g. of a 45—50% magnesium hydride are obtained.

What we claim is:—

- 20 1. A process for the production of hydrides of the metals calcium, strontium, barium, magnesium, lithium, sodium and potassium, wherein a carbide, cyanide, cyanamide, phosphide, silicide or boride of one of these metals is reacted with hydrogen under such conditions and for such a period that a substantial
25 amount of the hydride of the metal is formed.

2. A process for the production of hydrides of the metals calcium, strontium, barium, magnesium, lithium, sodium and potassium, where-

in a cyanamide of one of these metals is reacted with hydrogen under superatmospheric pressure.

3. A process as claimed in claim 1 or 2, wherein the metal compound to be subjected to the reaction with hydrogen is ground *in vacuo* or in an inert gas atmosphere and then subjected to the action of the hydrogen.

4. A process as claimed in claim 1, 2 or 3 wherein the reaction takes place in the presence of a catalytic quantity of N_2 , S, I_2 , NH_3 , H_2S , HI , HgI_2 , CaI_2 , MgI_2 , Na_2S , CaS or Na.

5. A process as claimed in any of claims 1 to 4, wherein the reaction takes place at a temperature of 500 — 800°C . and a pressure of 100—600 atm.

6. A process for the production of metallic hydrides, substantially as described with reference to any of the Examples.

7. Metal hydrides whenever produced by the process claimed in any of the preceding claims.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1958.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies may be obtained.

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